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The Crystal Structure of 5,5-Dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane Monohydrate

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The crystal structure of 5,5-dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane monohydrate (I) has been determined by the three dimensional X-ray diffraction method. The crystals belong to monoclinic system, with space group $P2_1$. The unit cell dimensions are; $a=9.50$, $b=5.86$, $c=8.31$ Å, $\beta=106°8'$, and two molecules per unit cell. The six-membered dioxaphosphorinane ring has a chair conformation, with P=O bond in equatorial position. The bond angles and distances of the phosphate group are similar to those found in the corresponding acyclic phosphates.

One of the most interesting roles of the molecular structure of nucleotide is the conformation around the phosphate linkage. Recently, the conformation of two naturally occurring nucleotides, inosine-5′-monophosphate and guanosine-5′-monophosphate, have been studied both in aqueous solution and in crystalline state by ^{31}P NMR measurements¹⁾ and X-ray diffraction method,²˒³⁾ respectively. The results, so far obtained, suggest that quite similar conformations of the phosphate fragment are preferred both in aqueous solution and in crystalline state.

Determination of the dihedral angle in P–O–C–H system by NMR method is based upon the dihedral angular sensitive nature of J_{POCH} (phosphorus-proton spin-spin coupling constant).¹˒⁴⁻⁶⁾ Thus, in order to determine the values of "*gauche*" and "*trans*" P–H coupling (Fig. 1) a variety of the conformationally fixed 1,3,2-dioxaphosphorinanes

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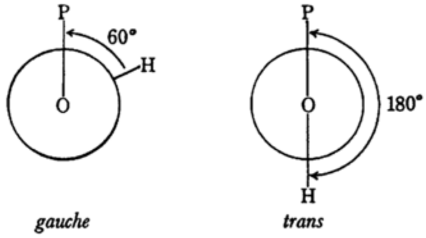

gauche *trans*

Fig. 1. Newman projection formulae (along O–C axis) for "gauche" and "trans" P–O–C–H group.

were studied by NMR.[1,4–6]

During the course of our NMR studies, we realized the necessity of knowing the actual dihedral angles and bond distances in 1,3,2-dioxaphosphorinanes.[5]

The present study gives further structural information about the six-membered cyclic phosphates, for only two of the derivatives (II[7] and III[8]) were studied by X-ray diffraction method. I is a particularly informative molecule for comparison with acyclic phosphoric acid esters and for the examination of preference of P=O bond at the equatorial bond.[7,8]

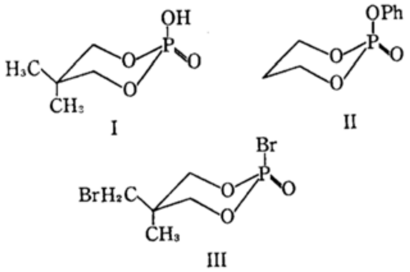

Fig. 2

Experimental

5,5-Dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane (I) can be obtained as either orthorhombic (α-form) or monoclinic crystals (β-form), when I is crystallized out from an aqueous solution. Crystal data of these two forms are given below.

α-form (orthorhombic; $P2_12_12_1$)
$a = 9.05,\ b = 6.08,\ c = 16.06$ Å,
$D_x = 1.38,\ Z = 4.$
β-form (monoclinic; $P2_1$)
$a = 9.50,\ b = 5.86,\ c = 8.31$ Å, $\beta = 106°8'$,
$D_x = 1.38,\ Z = 2.$

The structure determination by X-ray diffraction method was carried out with a crystal of the β-form. A needle-shaped crystal (elongated along the monoclinic b-axis) was mounted on a Weissenberg camera and rotated around its axis. Equi-inclination Weissenberg photographs for the five layer $0 \leq k \leq 4$ were recorded by multi-film technique with Cu$K\alpha$ radiation. The intensities were estimated visually. No corrections were made for absorption. The x and z coordinates of the phosphorus atom were determined readily from (u, 1/2, w) Harker section. The y parameter of the phosphorus atom was taken as zero. Three dimensional Fourier syntheses, based on the phase angles calculated from the position of phosphorus atom, revealed all the other peaks due to lighter atoms together with their mirror images. One set of the peaks could be picked out as real. The R-index at this stage was 0.33. Several cycles of block-matrix least squares refinements with isotropic temperature factors reduced R-index to 0.16, and following full-matrix least-squares refinements with isotropic temperature factors reduced R to 0.151. Finally, anisotropic temperature factors were introduced and several cycles of block-matrix least squares refinements were carried out. The weighting schemes at this step were $F_{\max}/|F_0|$ for $|F_0| > F_{\max}$, 1.0 for $F_{\min} < |F_0| < F_{\max}$ and 0.5 for $|F_0| < F_{\min}$, where $F_{\max} = 20.0$ and $F_{\min} = 7.0$. The final R-index was 0.127.

Table 1. The final positional parameters and their standard deviations (Å)

	x/c	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
P	0.1927	0.0027	0.0000	0.0000	0.3233	0.0030
O(1)	0.0889	0.0118	−0.1494	0.0176	0.2077	0.0112
O(2)	0.2824	0.0093	0.1679	0.0126	0.2474	0.0098
O(3)	0.3138	0.0102	−0.1394	0.0153	0.4574	0.0101
O(4)	0.1097	0.0087	0.1475	0.0145	0.4283	0.0097
O(5)	0.1540	0.0102	0.4652	0.0149	0.0512	0.0093
C(1)	0.4036	0.0115	0.0045	0.0253	0.6034	0.0141
C(2)	0.3055	0.0167	0.1211	0.0293	0.6964	0.0156
C(3)	0.2042	0.0163	0.2766	0.0250	0.5773	0.0158
C(4)	0.2213	0.0179	−0.0626	0.0260	0.7745	0.0173
C(5)	0.4109	0.0191	0.2549	0.0266	0.8312	0.0169

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8) T. A. Beineke, *Chem. Commun.*, **1966**, 860.

TABLE 2. THE FINAL ANISOTROPIC TEMPERATURE FACTORS

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	0.0061	0.0089	0.0095	0.0008	0.0008	−0.0010
O(1)	0.0128	0.0369	0.0139	−0.0072	−0.0013	−0.0054
O(2)	0.0084	0.0172	0.0138	−0.0017	0.0029	0.0032
O(3)	0.0086	0.0274	0.0142	0.0019	0.0006	−0.0018
O(4)	0.0068	0.0256	0.0136	0.0027	0.0027	−0.0020
O(5)	0.0137	0.0070	0.0130	0.0035	0.0008	0.0021
C(1)	0.0055	0.0340	0.0156	0.0097	0.0009	−0.0011
C(2)	0.0123	0.0387	0.0128	−0.0032	0.0014	−0.0025
C(3)	0.0113	0.0304	0.0141	0.0046	−0.0008	−0.0088
C(4)	0.0135	0.0427	0.0162	0.0016	0.0073	0.0098
C(5)	0.0164	0.0309	0.0126	−0.0077	−0.0010	−0.0038

The temperature factors are in the form

$$T=\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-2B_{12}hk-2B_{13}hl-2B_{23}kl)$$

TABLE 3. DESCRIPTION OF THERMAL ELLIPSOIDS

$B_i=8\pi^2U_i^2$, where U_i is the root mean square displacement corresponding to i axis of the ellipsoid.

C_{ia}, C_{ib}, C_{ic} are the direction cosines of the i axis with respect to the crystal axis.

Atom	Axis	B_i	U_i	C_{ia}	C_{ib}	C_{ic}
P	1	1.25	0.13	−0.1871	0.9780	0.0921
	2	1.93	0.16	0.7593	0.0845	0.6452
	3	2.93	0.19	−0.6232	−0.1906	0.7584
O(1)	1	2.07	0.16	0.5009	0.4520	0.7381
	2	5.30	0.26	−0.3648	−0.6630	0.6536
	3	6.35	0.28	0.7848	−0.5967	−0.1672
O(2)	1	2.03	0.16	0.4673	0.8482	−0.2493
	2	2.92	0.19	0.8103	−0.2980	0.5046
	3	3.96	0.22	−0.3537	0.4379	0.8265
O(3)	1	2.62	0.18	0.8220	−0.2580	0.5077
	2	3.43	0.21	−0.0689	0.8399	0.5384
	3	4.75	0.25	−0.5653	−0.4776	0.6726
O(4)	1	1.98	0.16	0.9298	−0.3641	0.0537
	2	3.27	0.20	0.1199	0.4378	0.8911
	3	4.16	0.23	0.3495	0.8221	−0.4507
O(5)	1	0.82	0.10	−0.1877	0.9661	−0.1771
	2	3.25	0.20	0.2667	0.2236	0.9375
	3	5.44	0.26	0.9453	0.1287	−0.2996
C(1)	1	0.75	0.10	−0.8617	0.4586	−0.2172
	2	3.92	0.22	0.0741	−0.3098	−0.9479
	3	6.37	0.28	−0.5021	−0.8329	0.2329
C(2)	1	1.83	0.15	0.7075	0.5850	0.3965
	2	3.59	0.21	−0.2949	−0.2654	0.9179
	3	7.54	0.31	0.6423	−0.7663	−0.0153
C(3)	1	2.24	0.17	0.0775	−0.6854	−0.7240
	2	3.04	0.20	−0.7857	0.4050	−0.4676
	3	6.91	0.30	−0.6137	−0.6051	0.5072
C(4)	1	2.43	0.18	0.5672	0.3708	−0.7354
	2	4.55	0.24	−0.8194	0.3445	−0.4582
	3	7.62	0.31	−0.0834	−0.8624	−0.4992
C(5)	1	2.17	0.17	0.4103	0.5343	0.7390
	2	4.37	0.24	−0.2089	−0.7338	0.6465
	3	7.26	0.30	0.8877	−0.4196	−0.1895

TABLE 4. BOND DISTANCES AND ANGLES

P–O(1)	1.457±0.014 Å	C(1)–C(2)	1.522±0.028 Å
P–O(2)	1.542±0.011	C(2)–C(4)	1.580±0.030
P–O(3)	1.582±0.012	C(2)–C(5)	1.494±0.016
P–O(4)	1.579±0.012	C(2)–O(5)	2.483±0.016
O(3)–C(1)	1.523±0.022	O(1)–O(5)	2.766±0.018
O(4)–C(3)	1.510±0.023		
O(1)–P–O(2)	117.8±0.8°	O(3)–C(1)–C(2)	112.3±2.0°
O(1)–P–O(3)	112.4±0.8	O(4)–C(3)–C(2)	112.3±2.0
O(1)–P–O(4)	110.1±0.8	C(1)–C(2)–C(3)	108.1±3.0
O(2)–P–O(3)	103.0±0.8	C(1)–C(2)–C(4)	109.9±3.0
O(2)–P–O(4)	106.5±0.8	C(1)–C(2)–C(5)	104.3±3.0
O(3)–P–O(4)	106.1±0.8	C(3)–C(2)–C(4)	111.5±3.0
P–O(3)–C(1)	114.2±1.2	C(3)–C(2)–C(5)	111.4±3.0
P–O(4)–C(3)	117.5±1.2	C(4)–C(2)–C(5)	111.4±3.0
		O(1)–O(5)–C(2′)	103.0±2.0

Results and Discussion

The crystal structure projected on *bc*-plane is shown in Fig. 3. The oxygen atom of the water molecule is located in the middle of the two phosphorinane molecules, which are separated from each other by one period along the *b*-axis and a hydrogen bond system is formed along this direction. The closest intermolecular distance is 3.42 Å between C(3)-atom of the one molecule and O(3)-atom of the neighboring molecule along the *b*-axis.

The bond distances and angles in the phosphate group are generally in good agreement with the corresponding values reported for some acyclic organic phosphates. For the sake of comparison, some reported values of P–O bond distances and O–P–O angles are listed in Table 5. It should be noted that the observed values of P–OR bond distance (1.58 Å) in I coincide with calculated values based on Cruickshank's rule for P–OR bonds in RPO_4^{2-} or $R_2PO_4^-$ groups.[9] Thus, it can be concluded that the six-membered cyclic phosphate forms an ordinal ester linkage similar to that in the acyclic phosphate.

The conformation of the molecule is a chair form carrying the P–OH in axial and P=O bond in equatorial position, respectively. In the previously reported two phosphorinanes (II and III), the P=O bonds are also in equatorial and P–OPh and –Br are in axial positions.[7,8] The P–O–C angles in

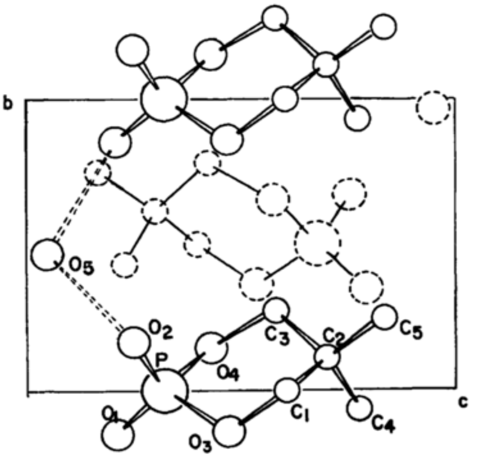

Fig. 3. Crystal structure of 5,5-dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane monohydrate. Projected along the *a*-axis.

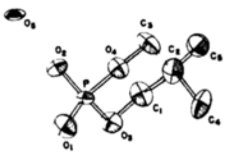

Fig. 4. Thermal vibrations of 5,5-dimethyl-2-oxo-2-hydroxy-1,3,2-dioxaphosphorinane monohydrate. The figure indicates that the atoms lie within the ellipsoids with 50% probability.

TABLE 5. BOND DISTANCES AND ANGLES OF ACYCLIC AND CYCLIC PHOSPHATES

Compound	Bond lengths (Å)				Bond angles (Å)				Ref.
	P=O	P–O⁻	P–OH	P–OR	O=P–OH	O=P–OR	OH–P–OR	OR–P–OR	
Dibenzyl phosphate	1.48		1.56	1.56, 1.57				103.8	a)
Di-*p*-chlorophenyl phosphate	1.497		1.49	1.579		106.5	109.7	108.1	b)
Barium diethyl phosphate		1.51		1.59, 1.62				103.5	c)
L-Serin phosphate	1.479	1.517	1.560	1.680					d)
2-Aminoethyl phosphate	1.493	1.503	1.557	1.591	109.8	103.9	106.2		e)
Cytidylic acid (orthorhombic)	1.483	1.504	1.551	1.611	113.6	10.1	101.5		f)
Cytidylic acid (monoclinic)	1.480	1.493	1.588	1.610	112.6	105.5	104.3		g)
Adenylic acid	1.495	1.514	1.566	1.610	106.4	105.7	106.5		h)
II	1.48			1.56, 1.57 1.59(–POh)		115.3 111.8(ring)		106.6 (ring)	7)
III	1.46			1.58 1.54		112.6 111.4		105.5	8)
I	1.465		1.546	1.597 1.597	117.8	112.4 110.1	106.5 106.1	106.1	

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b) M. Calleri and J. C. Speakman, *ibid.*, **17**, 1097 (1964).
c) Y. Kyogoku and Y. Iitaka, *ibid.*, **21**, 49 (1966).
d) H. G. McCallgm, J. M. Robertson and G. A. Sim, *Nature*, **184**, 1863 (1959).
e) J. Kraut, *Acta Cryst.*, **14**, 1146 (1961).
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g) C. E. Bugg and R. E. Marsh, *ibid.*, **25**, 67 (1967).
h) J. Kraut and L. H. Jensen, *Acta Cryst.*, **16**, 79 (1963).

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[9] D. W. J. Cruickshank, *J. Chem. Soc.*, **1961**, 5486.

TABLE 6. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

L	FO	FC
H,K= 0 0		
1*	294	360
2	223	220
3*	43	56
4*	87	79
5*	61	36
6*	0	2
7*	0	16
8	149	132
9*	68	54
H,K= 1 0		
0	143	168
1	161	194
2	106	90
3*	65	35
4*	96	80
5*	66	46
6*	0	14
7	150	138
H,K= 2 0		
0*	451	534
1	218	202
2	176	171
3	236	221
4	179	167
5	195	166
6*	73	55
7	105	103
H,K= 3 0		
0	232	193
1*	0	29
2*	88	55
3	194	186
4	172	167
5*	58	70
6*	84	83
7*	35	42
8*	73	71
H,K= 4 0		
0	141	132
1*	95	43
2	187	190
3*	0	10
4*	328	362
5	167	176
6*	30	31
7*	93	83
H,K= 5 0		
0*	0	14
1*	69	45
2*	89	65
3	215	230
4*	95	90
5*	0	24
6*	88	76
H,K= 6 0		
0*	0	11
1*	0	6
2*	97	91
3	174	177
4	165	151
5*	0	16
6*	86	69
7*	61	54
H,K= 7 0		
0*	0	3
1*	29	23
2*	99	97
3*	43	40
4*	41	51
5*	69	54
6*	33	14
H,K= 8 0		
0	128	126
1*	96	91
2*	0	6
3*	40	47
H,K= 9 0		
0*	0	2
3*	65	67
4*	32	43
H,K= 10 0		
0	161	137
2*	36	41
H,K= 1 0		
-1	246	269
-2*	99	94
-3	116	86
-4	167	155
-5	118	109
-6*	39	43
-7*	83	80
-8	127	123
-9*	41	43
-10*	29	42
H,K= 2 0		
-1*	465	592
-2	134	103
-3*	45	79
-4*	36	21
-5*	64	45
-6*	43	42
-7*	92	96
-8*	74	72
-9	123	116
-10*	48	40
H,K= 3 0		
-1	120	84
-2*	69	40
-3	164	155
-4*	30	33
-5	116	109
-6*	0	3
-7*	0	10
-8*	83	80
-9*	66	66
H,K= 4 0		
-1*	92	68
-2	119	117
-3*	75	87
-4*	310	324
-5	127	104
-6*	66	49
-7	130	136
-8*	52	51
H,K= 5 0		
-1*	31	36
-2*	44	33
-3*	57	56
-4	158	163
-5*	95	81
-6	109	109
-7*	71	79
H,K= 6 0		
-1*	53	47
-2*	35	32
-3*	73	47
-4	219	214
-5	263	316
-6*	42	19
-7	114	97
-8*	86	72
H,K= 7 0		
-1*	96	109
-2*	0	3
-3*	0	18
-4	118	124
-5*	52	44
-6*	43	69
-7*	81	84
-9*	38	44
H,K= 8 0		
-1*	42	36
-2	127	126
-3	125	133
-4*	0	32
-5	159	150
-6*	62	52
-7*	34	40
-8*	38	44
H,K= 9 0		
-1	117	109
-2	105	87
-3*	0	1
-4*	56	51
-5*	41	52
H,K= 10 0		
-1	173	148
-2*	49	42
-3	114	104
-4*	67	59
H,K= 11 0		
-1*	34	37
-2*	80	87
-3*	32	31
-5*	36	40
H,K= 1 1		
0*	493	607
1	187	167
2*	420	462
3	209	197
4*	58	43
5	119	118
6	117	103
7*	79	65
8*	57	61
H,K= 2 1		
0*	45	12
1*	310	340
2	124	130
3	202	191
4	109	99
5*	38	35
6	161	171
7*	83	78
8*	0	9
9*	49	61
H,K= 3 1		
0	104	69
1	191	167
2*	321	338
3	110	91
4	154	156
5	195	224
6*	50	57
H,K= 4 1		
0	119	85
1	143	128
2	125	104
3	129	112
4	153	159
5	110	86
6*	75	72
H,K= 5 1		
0*	72	47
1	145	132
2*	92	66
3*	100	91
4	182	203
5*	100	66
6	103	81
7*	67	58
H,K= 6 1		
0*	87	86
1*	47	46
2	175	191
3	116	123
4*	27	26
5*	94	87
6*	53	48
H,K= 7 1		
0*	76	58
1	124	123
2*	57	46
3*	55	49
4*	77	60
5*	64	61
6*	77	65
H,K= 8 1		
0*	62	67
1	119	122
2	123	109
4*	67	64
H,K= 9 1		
0	146	142
H,K= 10 1		
0*	0	9
1*	55	55
H,K= 11 1		
0*	77	72
H,K= 0 1		
-1	205	217
-2	248	225
-3	137	88
-4	143	112
-5*	90	88
-6*	97	109
-7	119	121
-8*	60	70
H,K= 1 1		
-1*	388	534
-2	159	136
-3	126	103
-4*	91	65
-5*	0	12
-6*	93	85
-7*	0	28
-8*	55	60
-9	105	111
H,K= 2 1		
-1	127	114
-2*	479	642
-3	206	155
-4*	81	49
-5*	96	78
-6*	0	13
-7*	44	51
-8*	66	73
-9*	61	65
H,K= 3 1		
-1*	56	61
-2	174	158
-3	194	166
-4	109	91
-5*	89	64
-6	148	130
-7	117	118
-8*	0	22
-9*	92	87
-10*	54	57
H,K= 4 1		
-1	121	79
-2	255	262
-3*	303	336
-4*	39	43
-5*	89	77
-6	121	132
H,K= 5 1		
-1	127	96
-2	112	86
-3*	85	66
-4	201	194
-5	189	193
-6*	0	26
-7	129	145
-8*	59	57
H,K= 6 1		
-1*	0	29
-2*	60	46
-3	139	125
-4*	89	77
-5*	59	54
-6	104	110
H,K= 7 1		
-1*	0	26
-2	138	126
-3	128	134
-4	102	88
-5	159	163
-6*	98	84
-7*	59	72
H,K= 8 1		
-1*	61	68
-2*	79	71
-3*	67	63
-4	107	100
-5*	41	44
-6*	48	40
-7*	89	85
H,K= 9 1		
-1*	70	62
-2*	86	70
-3	153	159
H,K= 10 1		
-1*	54	65
-2*	76	72
-7*	51	56
H,K= 11 1		
-1	105	94
-3*	67	56
-4*	35	41
H,K= 1 2		
0	111	98
1	191	173
2	161	153
3*	87	77
4	153	163
5*	49	42
6	108	105
7	172	157
H,K= 2 2		
0	141	126
1	180	177
2*	324	402
3	220	223
4	153	134
5*	82	64
6	115	120
7*	0	15
8*	51	60
H,K= 3 2		
0	196	211
1	196	211
2	115	104
3*	98	91
4*	30	33
5*	71	68
6	115	103
7*	72	50
8*	38	38
H,K= 4 2		
0*	60	40
1	207	226
2	166	156
3*	39	47
4	105	95
5*	40	30
6*	0	7
7*	97	84
H,K= 5 2		
0	202	211
1*	32	29
2	107	90
3	117	135
4*	49	51
5*	28	40
6*	77	71
H,K= 6 2		
0	110	112
1*	101	88
2*	95	88
3*	64	66
4*	45	34
5*	0	17
6*	98	83
H,K= 7 2		
0*	99	90
1*	91	79
2	161	200
3*	63	50
4*	64	51
5*	63	66
6*	48	63
H,K= 8 2		
0*	79	85
1*	71	68
2*	0	11
3*	73	68
4*	0	21
5*	41	41
H,K= 9 2		
0*	39	22
1	103	82
2*	93	83
3*	36	30
4*	49	57
H,K= 10 2		
0*	48	45
1*	0	9
2*	57	64
H,K= 0 2		
-1*	83	72
-2	104	81
-3	279	302
-4*	75	50
-5	137	125
-6	104	100
-7*	72	80
-8*	50	65
-9*	34	38
H,K= 1 2		
-1	273	246
-2	183	176
-3	157	153
-4	203	215
-5	159	156
-6*	49	36
-7	110	119
-8*	39	37
H,K= 2 2		
-1	142	120
-2*	79	59
-3	112	86
-4	208	213
-5*	96	97
-6	138	154
-7	102	87
-8*	44	51
-9*	44	57
H,K= 3 2		
-1	113	94
-2*	369	381
-3*	285	331
-4	107	85
-5	154	153
-6*	98	100
-8*	55	70
H,K= 4 2		
-1	211	225
-2*	70	62
-3*	78	59
-4	149	158
-5*	38	43
-6	105	99
-7	120	128
-8*	39	32
-9*	48	56
H,K= 5 2		
-1	156	160
-2	146	135
-3	177	161
-4*	98	56
-5	109	102
-6*	55	54
-7*	63	49
H,K= 6 2		
-1	158	161
-2	174	178
-3*	66	46
-4*	66	64
-5*	90	96
-6*	0	17
-7*	54	48
-8*	60	58
H,K= 7 2		
-1	149	151
-2*	0	15
-3*	83	71
-4*	86	80
-5*	45	36
-6*	55	42
-7*	51	40
-9*	43	63
H,K= 8 2		
-1*	0	33
-2	143	147
-3	135	128
-4*	0	14
-5*	75	79
H,K= 9 2		
-1*	53	54
-2*	0	31
-3*	0	18
-4*	39	58
-5*	42	41
-6*	36	33
-7*	65	67
-8*	30	46
H,K= 10 2		
-1*	76	70
-2*	0	8
-3*	82	59
-4*	61	49
-5*	0	24
-6*	45	51
H,K= 11 2		
-2*	62	45
-5*	79	74
H,K= 1 3		
0	109	91
1*	93	80
2	188	164
3	166	163
4*	84	64
5	116	118
6*	76	81
H,K= 2 3		
0*	77	60
1	145	138
2*	80	64
3	107	95
4	105	95
5*	0	22
6	124	97
7*	45	45
H,K= 3 3		
0	108	90
1	157	147
2	157	141
3*	32	53
4*	43	46
5*	61	79
6*	0	44
8*	66	84
H,K= 4 3		
0	253	288
1	210	212
2	103	97
3*	38	27
H,K= 5 3		
0*	55	48
1	160	165
2*	0	19
3*	48	61
4*	39	57
5*	0	6
6*	57	50
7*	44	55
H,K= 6 3		
0	211	243
1*	0	17
2	107	118
3*	0	29
4*	0	17
5*	61	65
H,K= 7 3		
0*	63	69
1*	79	99
2*	0	21
3*	25	50
4*	45	60
H,K= 8 3		
0*	0	28
1*	99	104
2*	92	87
3*	0	22
4*	74	80
H,K= 9 3		
0*	49	63
2*	39	41
3*	65	83
H,K= 10 3		
1*	38	52
H,K= 0 3		
-1	116	104
-2	112	103
-3	144	116
-4	245	248
-5	187	219
-6*	79	88
-7*	77	78
H,K= 1 3		
-1	103	96
-2	111	93
-3	163	169
-4	179	173
-5	114	107
-6	131	156
H,K= 2 3		
-1*	60	58
-2*	359	228
-3*	86	67
-4	144	132
-5*	387	255
-6*	93	81
-7*	60	81
H,K= 3 3		
-1	141	137
-2	129	128
-3	122	113
-4	116	99
-5	106	104
-6	126	120
-7*	63	58
H,K= 4 3		
-1	132	120
-2	170	178
-3	171	173
-4*	0	9
-5*	53	46
-6*	61	60
-7*	39	53
-8*	33	51
H,K= 5 3		
-1	171	189
-2	176	193
-3*	35	25
-4*	45	49
-5*	39	26
-7*	67	67
H,K= 6 3		
-1	178	201
-2*	33	15
-3	122	116
-9*	43	69
H,K= 7 3		
-1*	56	58
-2	133	142
-3*	76	62
H,K= 8 3		
-1*	69	59
-2*	56	39
-3*	39	47
-4*	52	39
-7*	49	64
H,K= 9 3		
-3*	63	64
-6*	52	68
H,K= 10 3		
-4*	81	71
-5*	74	67
H,K= 1 4		
0*	27	36
1*	84	67
2*	100	77
3	141	135
4	183	199
5*	42	37
6*	51	43
7*	70	80
H,K= 2 4		
0*	100	99
1*	87	74
2	152	108
3	142	145
4*	65	73
5*	65	69
H,K= 3 4		
0	188	203
1	183	156
2*	41	36
3	105	114
4*	0	12
5*	0	24
6*	54	58
H,K= 4 4		
1*	87	76
2	111	109
3*	42	34
4*	60	79
H,K= 5 4		
0	225	253
1*	75	62
2*	47	43
3*	47	57
6*	43	64
H,K= 6 4		
0*	63	53
1*	76	85
2*	0	35
3*	63	69
H,K= 7 4		
0*	81	59
1*	46	47
2*	92	86
3*	54	52
4*	50	45
H,K= 8 4		
0*	75	65
1*	70	65
2*	0	13
3*	66	76
H,K= 9 4		
0*	34	45
1*	46	53
2*	48	59
H,K= 0 4		
-1*	83	58
-2*	52	49
-3	154	169
-4	108	100
-5*	59	58
-6*	88	91
H,K= 1 4		
-1*	86	20
-2*	83	66
-3*	54	60
-4	210	240
-5	183	157
-6*	0	6
-7*	68	65
H,K= 2 4		
-1	134	119
-2*	51	53
-3	149	127
-4	149	144
-5*	0	5
-6*	60	69
-7*	85	84
H,K= 3 4		
-1*	91	69
-2	127	117
-3	134	122
-4*	27	14
-5	136	125
-6*	56	40
-7*	45	47
-8*	46	66
H,K= 4 4		
-1	171	169
-2	131	117
-3*	98	87
-4	105	96
-5*	0	4
-6*	0	38
-7*	67	82
-8*	32	42
H,K= 5 4		
-1	174	153
-2*	82	74
-3*	91	88
-4*	71	70
-8*	66	68
H,K= 6 4		
-1*	76	83
-2*	84	99
-3*	55	44
-4*	47	45
-5*	22	48
-8*	46	71
H,K= 7 4		
-2*	0	20
-3*	70	49
-4*	66	70
H,K= 8 4		
-1*	0	13
H,K= 7 4		
-1	130	141
H,K= 8 4		
-2*	79	62
-3*	59	57
-4*	0	18
-5*	48	71
H,K= 9 4		
-4*	76	75
-5*	56	50

the phosphorinane ring are fairly large compared with the C–C–C angle of 111° in cyclohexane.[10) Beineke[7) also pointed out that the phosphorinane rings are somewhat more flattened than the cyclohexane ring, and suggested such ring-deformation causes the reduction of the steric repulsion between the axial substituent at the phosphorus atom and the hydrogen atom at 1,3-diaxial position.

It is of interest that the S=O bond in the cyclic sulfite of 1,3-propanediol tends to favor the axial position.[11) The dihedral angle in P–O–C–C system in I is about 55°, which is considerably smaller than the dihedral angle in a strict *gauche* conformation (60°).

All of the crystallographic computations were carried out on a CDC 3600 computor with the UNICS crystallographic system programs.[12)

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10) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

11) H. F. Van Woerden and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **86**, 341 (1967) and references cited therein.

12) *UNICS* program system, edited by T. Sakurai, Crystallographic Association of Japan (1967).